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COMMUNICATION

Effect of the Delay Time on Photoelectron Spectra and State Populations of Nonadiabatic Coupling Molecule

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Abstract: The influence of the delay time on the wave packet motion of NaI molecule was studied by intense femtosecond pump-probe pulses via time-dependent wave packet approach. The delay time dependence of state populations was studied firstly. Wave packet moves periodically with oscillation period 1000 fs. The wave packet reaches the crossing point at 200 fs firstly and at 800 fs secondly, and bifurcates. The periodical motion of the wave packet induces the periodical variation of photoelectron spectra. The wave packet bifurcation affects state populations. The results show the wave packet motion and selective distribution of state populations can be achieved by adjusting pump-probe delay time. The results can provide some important basis for realizing the optical control of molecules experimentally.

AMS subject classifications: 70F05, 65M22

Keywords: Intense femtosecond pump-probe pulse, State populations, Wave packet motion, Photoelectron spectra

Introducation

With the development of ultrashort and ultrastrong laser pulse technology, more and more researches have focused on the control of molecular dynamics in real time. Controlling the evolution of wave packet will be a benefit for light manipulation of molecular processes experimentally. The photoelectron spectra and state populations map the wave packet dynamic information of the electronic state, are found to be sensitive to the parameters of

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the laser fields, and have been studied in multi-level molecular systems [1-14].

NaI molecule is a typical molecule with a avoided crossing between two nonadiabatically coupled electronic states at internuclear distance 7 Å, and has been studied experimentally and theoretically. Braun et al. [1] and Charron and Suzor-Weiner [2] presented that the wave packet moves periodically on the electronic state potentials of NaI molecule, which induces the periodical variation of photoelectron spectra. Yao et al. [3,4] suggested that the first dissociation probability decreases with increasing pump wavelength. The photoelectron spectra are dependent on the delay time. Arasaki et al. [5-7] indicated that the total ion signal oscillates periodically with increasing delay time. Miao et al. [8,9] and Liu et al. [10] suggested that the delay time affects state populations and photoelectron spectra. Ma et al. [11] presented that the pump wavelength affects state populations. Zhao et al. [12] studied the influence of field-free orientation on the predissociation dynamics of the NaI molecule. Xiong et al. [13] presented that the wavelength affects state populations of CsI molecule. Zhu et al. [14] suggested that the delay time affects state populations of CsI molecule.

The Photoelectron spectra reflect the excited state dynamics; however, the effect of the delay time on state populations of NaI molecule has not been reported. This paper presents new data on the influence of delay time on the photoelectron spectra and state populations driven by pump-probe pulses via time-dependence quantum wave packet method.

Formalism

Three states (the ground state *X*, the excited state *A* and the ion ground state *I*) are involved in the multiphoton ionization of NaI molecule [1-3], as shown in **Figure 1**. The molecule initially populated in ground state *X* is resonantly excited to the excited state *A* by pump laser pulse with a central wavelength of $\lambda_1 = 328$ nm, then the excited molecule is ionized by probe laser pulse with a central wavelength of $\lambda_2 = 228$ nm after the time delay, and the emitted photoelectron is detected from *I*.

The wave function for the three-state model can be written as

$$\boldsymbol{\Psi} = (\psi_X, \psi_A, \boldsymbol{\psi}_I)^{\mathrm{T}}, \tag{1}$$

Where ψ_X, ψ_A and $\boldsymbol{\psi}_I$ are the wave functions for the states *X*, *A*, and *I*, respectively. The ion ground state *I* is a continuum state and can be discretized into a band of quasicontinuum states. The ψ_I can be further expressed as

$$\boldsymbol{\psi}_I = (\psi_1, \psi_2, ..., \psi_N)^{\mathrm{T}}, \tag{2}$$

where *N* represents the number of discrete states of NaI ion. The wavefunctions $\boldsymbol{\psi}_I$ within